Nonadiabatic Molecular Dynamics Simulations: Synergies between Theory and Experiments

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CONSPECTUS: Recent developments in nonadiabatic dynamics enabled *ab inito* simulations of complex ultrafast processes in the condensed phase. These advances have opened new avenues in the study of many photophysical and photochemical reactions triggered by the absorption of electromagnetic radiation. In particular, theoretical investigations can be combined with the most sophisticated femtosecond experimental techniques to guide the interpretation of measured time-resolved observables. At the same time, the availability of experimental data at high (spatial and time) resolution offers a unique opportunity for the benchmarking and the improvement of those theoretical models used to describe complex molecular systems in their natural environment. The established synergy between theory and experiments can produce a better understanding of new ultrafast physical and chemical processes at atomistic scale resolution. Furthermore, reliable *ab inito* molecular dynamics simulations can already be successfully employed as predictive tools to guide new experiments as well as the design of novel and better performing materials.

In this paper, I will give a concise account on the state of the art of molecular dynamics simulations of complex molecular systems in their excited states. The principal aim of this approach is the description of a given system of interest under the most realistic ambient conditions including all environmental effects that influence experiments, for instance, the interaction with the solvent and with external time-dependent electric fields, temperature, and pressure. To this end, time-dependent density functional theory (TDDFT) is among the most efficient and accurate methods for the representation of the electronic dynamics, while trajectory surface hopping gives a valuable representation of the nuclear quantum dynamics in the excited states (including nonadiabatic effects). Concerning the environment and its effects on the dynamics, the quantum mechanics/molecular mechanics (QM/MM) approach has the advantage of providing an atomistic (even though approximated) description of the solvent molecules, which is crucial for the characterization of all ultrafast relaxation phenomena that depend on the geometrical arrangement at the interface between a molecule and the solvent, for example, the hydrogen bond network.

After a short description of the TDDFT-based implementation of Ehrenfest and trajectory surface hopping dynamics, I will present applications in different domains of molecular chemistry and physics: the analysis and the understanding of (time-resolved) X-ray absorption spectra, the interpretation of the ultrafast relaxation dynamics of photoexcited dyes in solution, and the design of specific laser pulses (capable of inducing desired chemical reactions) using local control theory.
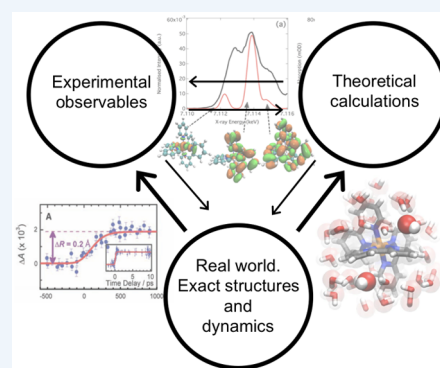
INTRODUCTION

The understanding of the ultrafast dynamics of reactive matter (with or without the effect of external electromagnetic fields) requires accurate experimental and theoretical investigations. From the experimental side, modern radiation sources like the free electron lasers (FEL) will give an important contribution providing very intense pulses with a time resolution (pulse length) of the order of a few femtoseconds. This will give the opportunity to study the dynamics of a number of physicochemical processes with unprecedented space and time resolutions. However, due to the extreme conditions under which these experiments will be carried out (extreme intensities and very short collecting times), the interpretation of the monitored signals will require special care. In particular, the

reconstruction of the three-dimensional atomic structure of the system under investigation and its dynamics will necessarily require adequate computational and numerical tools. Among these, first-principles nonadiabatic dynamics will offer the possibility to "simulate" by solving numerically the fundamental equations of motion (the time-dependent Schrödinger equation) the time evolution of molecular and solid state systems at atomistic scale with arbitrarily small time resolution. The interplay between ultrafast experiments and first-principle simulations will therefore become crucial for an optimal understanding of the fundamental nature of most ultrafast

physicochemical processes. The large efforts invested in the development of these experimental and theoretical tools will be largely compensated by the "new physics" and the "new chemistry" that will be disclosed at the most fundamental level.

The Mapping Problem

In general, experiments detect a low-dimensional (time-dependent) signal corresponding to a given chemical or physical process of interest. After the collection of the experimental data, the main difficulty consists in "translating" this information into a time-resolved three-dimensional picture of all atoms involved in the process (solute and solvent). In fact, while the mapping that relates a given structure to the measured observable is generally unique, the inverse relation is not; in the most general case, the same recorded experimental spectrum can correspond to different physical structures. Obviously, exceptions to this situation exist, for instance, when time allows for an accurate determination of an X-ray crystallographic structure. However, this is in general not possible when dealing with ultrafast measurements. Theory and in particular *ab initio* MD simulations can therefore become essential tools for the solution of this mapping problem: the knowledge of the detailed atomistic structure at any time can be used to reconstruct the experimentally detected observables shedding new light into the complex mapping between measured observables and corresponding molecular structures. One way to achieve this result consists in the simulation of the experimental conditions by means of time-dependent *ab initio* molecular dynamics calculations. The most recent developments in the field of nonadiabatic molecular dynamics[1−5] allow for an accurate simulation of the extreme conditions met in ultrafast experiments such as pump−probe studies. In particular, we are nowadays in the position of reproducing in our calculations the interaction of time-dependent electric field with the electronic structure of complex molecular systems composed by several hundreds of atoms and describing the subsequent time evolution of the resulting photoexcited complexes for several picoseconds with a time resolution of a few attoseconds. Depending on the nature of the physical process under investigation, the dynamics can be either restricted to the electronic degrees of freedom (for instance, in ultrafast electronic relaxations following photoelectron ionizations) or, most commonly, extended to the correlated electron−nuclear motion. Very important for the simulation of a process under *realistic* experimental conditions is also the correct treatment of the environment. To this end, different solutions have been proposed, among which the implicit solvation model,[6,7] where the solvent is replaced by a continuum uniform dielectric, and the explicit representation of the solvent by means of fully atomistic or coarse grained models are the most commonly used. Once a clear match is established between measured and computed observables this can also be used to refine the approximations inherent to any molecular dynamics approach for large molecular systems, including improvements of the electronic structure (mainly density functional theory (DFT) and time-dependent density functional theory (TDDFT) functionals and linear response kernels), of the description of the nuclear quantum effects (wavepacket branching and dephasing), and of the interaction with the environment (QM/MM coupling).

The Accuracy Problem in the *Direct* Simulation of the Dynamics

While experiments of the type described above (e.g., pump−probe) are designed to provide an *indirect* measurement of the complex molecular dynamics at atomistic scale, the *direct* simulation of the system of interest (with or without the external perturbation induced in the experiment) can provide the desired information at the required spatial and time resolution. The step toward a theoretical modeling of the fundamental processes at atomistic scale without the support of any experimental observation is limited by the *accuracy* problem intrinsic to all approximate solutions to the time-dependent many-body molecular Schrödinger equation (here with molecular we stress the dependence of the system wave function from both nuclear and electronic coordinates). Approximations in *ab initio* molecular dynamics simulations are twofold: first, one can transform the original system Hamiltonian into a new form more suited for a numerical solution. This is, for instance, the case in DFT/TDDFT where the complex interacting Hamiltonian is mapped (in principle in an exact way) into a system of noninteracting particles subject to a compensating local external potential (the exchange−correlation (xc) potential) for which we need to find valid approximations. More extreme approximations of the Hamiltonian are obtained in the so-called semiempirical methods.[5] Other approximations use the exact Hamiltonian combined with approximated expansion of the many-electron wave functions. These methods comprise configuration interaction (CI) approaches, multiconfigurational self-consistent field (CASSCF) with or without corrections to include dynamical correlation (Møller−Plesset perturbation), coupled cluster (CC), and many other post-Hartree−Fock methods. The situation becomes even more complex when, in addition to the approximations of the electronic part of the Schrödinger equation, one also considers nuclear quantum effects, which are of particular relevance in nonadiabatic dynamics.[4] The second important source of approximations is linked to numerics. Despite the enormous increase of computational resources in the last decades, the unfavorable scaling associated with most electronic structure approaches hampers an adequate sampling of the electronic wave function space in both the ground and excited states. When it comes to *ab initio* dynamics, the situation becomes even more critical since the numerical costs associated with the evaluation of energies and forces are multiplied by the number of time steps required to describe the process of interest. In general, ground state simulations based on DFT are limited to tens of picoseconds while nonadiabatic simulations can rarely be pushed over 1 ps. These approximations raise inevitably the issue about the *predictivity* of *ab initio* molecular dynamics simulations. Unfortunately, there is no way to predict *a priori* the effects of the approximations introduced at the level of the Hamiltonian or for the description of the many-electron wave function, and therefore a number of tests have to be performed to assess the quality of the xc-functional in DFT, the many-electron wave function representation in the post-Hartree−Fock, and the basis set used in the expansion of the molecular orbitals. These quality checks are usually performed using very accurate single point calculations as references (when affordable) or, even better, experimental results. A word of caution is however required when comparing experimental and numerical results. Due to the difficulties in controlling the experimental conditions, the match with the numerical calculations can be

often problematic: effects related to the environment, sample size, pressure, and temperature are difficult to reproduce in a simulation and will always give a margin of uncertainty.[8]

Predictivity of *ab Initio* Simulations

Despite all approximations inherent to any *ab initio* dynamics of complex molecular systems, in some cases the level of accuracy is such that these theoretical approaches can be used to guide the interpretation of experiments and the design of new materials.[9,10] This is in my opinion the main challenge that computational physics and chemistry have to face in the near future: moving from the realm of the "potentiality" to the one of the "predictivity". In addition, *ab initio* (adiabatic and nonadiabatic) molecular dynamics simulations can also be used to predict the feasibility of new experiments before the realization of the required instruments. This will give the opportunity to best guide the efforts of the experimentalists toward the most successful experimental setups and the optimization of the experimental parameters and conditions.

■ FIRST-PRINCIPLES NONADIABATIC DYNAMICS WITH DFT AND TDDFT

Quantum Dynamics

Dynamics in the excited states requires, in addition to the solution of the Schrödinger equation for the electronic structure, a quantum mechanical treatment of the nuclear degrees of freedom. In fact, effects like wavepacket branching on different potential energy surfaces (PESs) and nonadiabatic effects at avoided crossings and conical intersections have no classical equivalent and require a quantum mechanical description of the nuclear degrees of freedom. Several methods have been developed for the numerical solution of the quantum dynamics. Some are conceived for the investigation of nuclear quantum effects in a reduced number of collective nuclear degrees of freedom for which PES can be precomputed.[11] However, in the framework of atomistic *ab initio* nonadiabatic molecular dynamics simulations, the use of trajectory-based solutions of the nuclear quantum dynamics can be easily combined with an efficient on-the-fly calculation of all necessary electronic structure quantities without the need to restrict the configuration space to a small subset of collective variables. In addition, atomistic trajectory-based solutions to the quantum dynamics have also the advantage of being easily coupled to external fields[1,2,4] (electromagnetic radiations) and to a molecular description of the environment (solvents, protein matrices, solid bulk phase, and others). It is important to mention that the cost of approximating the true wavepacket dynamics with a swarm of classical trajectories is the neglect of a rigorous description of some nuclear quantum effect, for instance, the tunneling of light elements.

Trajectory-Based Quantum Dynamics

The intuitively appealing picture of trajectories hopping between coupled potential energy surfaces gave rise to a number of quasiclassical implementations of quantum dynamics. The most well-known method is Tully's "fewest switches" trajectory surface hopping (TSH),[12] which has evolved into successful and widely used techniques.[1,4,5] In recent years, the term surface hopping and its underlying ideas have also been used in the derivation of multiple spawning[3] and the stochastic modeling of deterministic differential equations, for example, in the quantum-classical Liouville approach. Alternatively, with the Bohmian (or hydrodynamical) description of quantum

mechanics, it is possible to derive formally exact equations of motion for quantum trajectories representing the dynamics of volume elements in configuration space.[13,14]

Another interesting solution of the nuclear quantum dynamics is the so-called multiconfiguration time dependent Hartree approach (MCTDH).[11] By its very nature, this approach requires the computation of all relevant PESs and corresponding couplings before the actual propagation of the nuclear wavepacket. This clearly implies an important computational effort that limits the applicability of this method to a limited number of degrees of freedom (from 1 to ~10).[15] In addition, the determination of the relevant degrees of freedom to include in the dynamics can also become a challenging problem, which requires some *a priori* knowledge of the most relevant vibrational modes involved in the process of interest. However, it is important to mention that the recent development of *on-the-fly* methods within the MCTDH framework will probably soon allow some relaxation of these limitations.[16]

TDDFT-Based Nonadiabatic Dynamics with Trajectories

We begin our discussion by introducing the time-dependent Schrödinger equation (TDSE) for a molecular system

$$i\hbar\partial_t\Psi(\mathbf{r}, \mathbf{R}, t) = \hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}, t) \tag{1}$$

where $\Psi(\mathbf{r},\mathbf{R},t)$ is the total wave function of the system, which depends on the electronic and nuclear collective coordinates $\mathbf{r} = (r_1,\dots,r_i,\dots,r_{N_{el}})$ and $\mathbf{R} = (R_1,\dots R_\gamma,\dots R_{N_n})$. In eq 1, $\hat{H}(\mathbf{r},\mathbf{R})$ is the molecular Hamiltonian given by

$$\hat{H}(\mathbf{r}, \mathbf{R}) = -\sum_\gamma \frac{\hbar^2}{2M_\gamma}\nabla_\gamma^2 - \sum_i \frac{\hbar^2}{2}\nabla_i^2 + \sum_{i<j}\frac{1}{|r_i - r_j|}$$
$$- \sum_{\gamma,i}\frac{Z_\gamma}{|R_\gamma - r_i|} + \sum_{\gamma<\zeta}\frac{Z_\gamma Z_\zeta}{|R_\gamma - R_\zeta|} \tag{2}$$

Ehrenfest Dynamics. Ehrenfest dynamics (EHD) is derived using the following ansatz for the molecular wave function

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{r}, t)\Omega(\mathbf{R}, t)\exp\left[\frac{i}{\hbar}\int_{t_0}^t \mathrm{d}t'\, E_{el}(t')\right] \tag{3}$$

which, when inserted in eq 1, gives (in the classical $\hbar \to 0$ limit for the nuclear wave function) the following equations of motion for (classical) nuclei and electrons[17,18]

$$M_\gamma\ddot{\mathbf{R}}_\gamma(t) = -\nabla_\gamma\langle\hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})\rangle \tag{4}$$

$$i\hbar\partial_t\Phi(\mathbf{r}, t) = \hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})\Phi(\mathbf{r}, t) \tag{5}$$

where

$$\langle\hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})\rangle = \int \mathrm{d}\mathbf{r}\, \Phi^*(\mathbf{r}, t)\hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})\Phi(\mathbf{r}, t),$$
$$E_{el}(t) = \iint \mathrm{d}\mathbf{r}\, \mathrm{d}\mathbf{R}\, \Phi^*(\mathbf{r}, t)\Omega^*(\mathbf{R}, t)\hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})\Phi(\mathbf{r}, t)$$
$$\Omega(\mathbf{R}, t) \tag{6}$$

and $\hat{\mathcal{H}}_{el}(\mathbf{r}, \mathbf{R})$ is given by the three central terms in eq 2. In eq 3, $\Phi(\mathbf{r},t)$, which depends parametrically on $\mathbf{R}(t)$, corresponds to the electronic wave function and $\Omega(\mathbf{R},t)$ to the nuclear one. Finally, using the Runge–Gross theorem,[19] we can *density functionalize* the electronic time dependent Schrödinger

equation (eq 5), which becomes (in the adiabatic limit for the TDDFT kernel[20,21])

$$i\hbar\partial_t\phi_i(\mathbf{r}, t) = -\frac{1}{2}\nabla^2\phi_i(\mathbf{r}, t) + V_{KS}(\{\phi_i(\mathbf{r}_i, t)_{N_{el}}\}, \mathbf{R})\phi_i(\mathbf{r}, t)$$

(7)

where $\{\phi_i(\mathbf{r},t)_{N_{el}}\}$ is the set of time-dependent Kohn–Sham (KS) orbitals corresponding to the initial conditions $\{\phi_i(\mathbf{r},0)_{N_{el}}\}$ and V_{KS} is the KS potential evaluated at the density $\rho(\mathbf{r},t) = \sum_i |\phi_i(\mathbf{r},t)|^2$.

Tully's Trajectory Surface Hopping. Starting from the Born–Huang expansion of the molecular Hamiltonian

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{i=1}^{\infty} \Omega_i(\mathbf{R}, t)\Phi_i(\mathbf{r}; \mathbf{R})$$

(8)

and passing to the classical limit for the nuclei, J. Tully derived the following set of equations for the coefficients (state amplitudes), $C_j^{[\alpha]}(t)$, that replace the quantum nuclear wave functions $\Omega_i(\mathbf{R},t)$,[12]

$$i\hbar\dot{C}_j^{[\alpha]}(t) = \sum_{i=1}^{\infty} C_i^{[\alpha]}(t)(E_i^{el}(\mathbf{R}^{[\alpha]})\delta_{ij} - i\hbar\sum_{\gamma}^{N_n} \mathbf{d}_{ji}^{\gamma}(\mathbf{R}^{[\alpha]})\cdot\dot{\mathbf{R}}_{\gamma}^{[\alpha]})$$

(9)

where $\Phi_i(\mathbf{r};\mathbf{R})$ are the adiabatic solutions of the time-independent electronic Schrödinger equation with fixed nuclear positions, and $\mathbf{d}_j^{\gamma}(\mathbf{R}) = \int d\mathbf{r}\ \Phi_j^*(\mathbf{r};\mathbf{R})\nabla_{\gamma}\Phi_i(\mathbf{r};\mathbf{R})$ are the nonadiabatic coupling vectors (NACV). A rigorous formulation of NACVs within linear response TDDFT is given in refs 22 and 23. Note that in the expansion in eq 8, the electronic state wave functions depend only implicitly on time through the nuclear coordinates, $\mathbf{R}(t)$, which, according to Tully's prescription, evolve "adiabatically" on a given PES j until a *hop* to a different surface i occurs with a probability that is computed from the state amplitudes $\{C_i^{[\alpha]}(t)\}$.[24] Tully's surface hopping is a multitrajectory approximation of the exact nuclear dynamics, and it is the ensemble of trajectories (labeled by the superscript $[\alpha]$) that ultimately describe the semiclassical time-evolution of the nuclear wavepacket.

The *density functionalization* of Tully's TSH was done in ref 25 and consists in the calculation of the state energies, $E_i^{el}(\mathbf{R}^{[\alpha]})$ with TDDFT and in the description of the nonadiabatic vectors, $\mathbf{d}_{ji}^{\gamma}(\mathbf{R})$ in terms of a set of auxiliary many-electron wave functions made of singly excited KS Slater determinants.[25,26] All necessary quantities for the propagation of the nonadiabatic dynamics within TSH can therefore be evaluated *on-the-fly* using TDDFT, which provides an advantageous balance between accuracy and numerical efficiency.

Finally, recent developments in the calculation of spin–orbit couplings in the framework of linear-response TDDFT[27] have offered the possibility to extend TDDFT-based TSH to the study of the nonadiabatic dynamics with intersystem crossings (ISC) between electronic states with different spin multiplicity.

Coupling to the Environment

The TDDFT/MM Coupling Scheme. The dynamics described so far does not include the coupling with the external environment, and therefore it can mainly by applied to the simulation of experiments performed under vacuum conditions. However, most of the interesting photophysical and photochemical reactions occurs in direct contact with their surroundings, and therefore an adequate description of the coupling between the photoexcited molecule and its environ-

ment is of crucial importance for a detailed (qualitative and qualitative) understanding of the photoprocess at atomistic scale. This interaction can be of different nature including electrostatic effects, spatial confinement, or intermolecular photochemical reactions with the surroundings (e.g., the solvent, a solid interface, or a protein matrix). The simplest and more rigorous approach consists in including part of the environment (typically two or three solvation shells) in the *ab initio* setup. This has the clear advantage that the coupling between the system of interest and its immediate surroundings can be described at the same level of theory (in this case DFT/TDDFT), allowing for a correct description of phenomena like photoinduced intermolecular charge transfer reactions. However, the large number of additional atoms added to the DFT/TDDFT calculation makes this type of simulations computationally very expensive, limiting therefore the affordable time scales to a few hundreds of femtoseconds. In addition, in order to avoid the problems associated with the presence of a solvent–vacuum interface,[28] periodic boundary conditions are usually required. Alternatively, instead of treating solvent molecules as part of the quantum setup, classical force fields can be used to describe the environment within a molecular mechanics approach.[29,30] The molecule of interest is still modeled at a quantum mechanical level (QM part), whereas the environment is described at a classical level (MM part) and no charge transfer between the two subsets is possible. Within this QM/MM approach, a complete solvation of the QM part can be achieved at a very low computational cost. Effects related to the solvent polarization can also be included, at least approximately, using polarizable force fields. For completeness, I need also to mention implicit solvent models in which the solvent is described by a dielectric continuum with a suitable dielectric constant modeling the macroscopic effects of the environment. In this case, the atomistic details of the solvent molecules are missing and, as a consequence, the effects of the hydrogen-bonding network at the interface between the molecule and the solvent cannot be reproduced. Furthermore, implicit solvent models for excited states dynamics should also account for the different electronic and nuclear relaxation times, with the latter being (in general) much longer than the former. Accounting for the progressive involvement of the nuclear relaxation during the first ultrafast (sub-picosecond) events that follow photoexcitation is still a major challenge for the development of new and more reliable implicit solvent models.

External Time-Dependent Fields. The coupling with an external time-dependent electric field is obtain by substituting the momentum operator $\hat{\mathbf{p}} = -i\hbar\nabla_r$ with the term $(\hat{\mathbf{p}} - e/c\mathbf{A}(\mathbf{r},t))$ in eq 2, where $\mathbf{A}(r,t)$ is the classical vector potential and $\mathbf{E} = -(1/c)\partial_t\mathbf{A}(t)$.[31] In TSH, in the presence of an external radiation field, the differential equation for the population coefficients in eq 9 acquires an additional term of the form: $i\omega_{ji}(A(t)/c)\epsilon^{\lambda}\cdot\boldsymbol{\mu}_{ji}(\mathbf{R}(t))$, which represents the interaction matrix element $\langle\hat{H}_{int}\rangle_{ji} = i\omega_{ji}(A(t)/c)\cdot\boldsymbol{\mu}_{ji}$ between states i and j with $\mathbf{A}(t) = A(t)\epsilon^{\lambda}$, $\boldsymbol{\mu}_{ji} = -\langle\Phi_j|\sum_{i=1}^{N_{el}}\hat{\mathbf{r}}_i|\Phi_i\rangle$, and $\omega_{ji} = (E_j - E_i)/\hbar$. Also in this case, auxiliary many-electron wave functions are used to evaluate all required matrix elements within the TDDFT framework.

Local Control and Pulse Design. Of particular interest is the possibility to design laser pulse sequences able to induce specific chemical modifications in a molecular system of interest. Several optimal control schemes have been developed with the aim at controlling chemical reactions. Among the most simple theoretical approaches, the *local control algorithm* has the

advantage of being numerically very efficient and easy to implement in TSH-based nonadiabatic dynamics schemes.[32−34] Briefly, one can easily show that an external time-dependent electric field of the form

$$\mathbf{E}^{[\alpha]}(t) = \pm\lambda \sum_j \mathcal{I}[C_i^{[\alpha]*}(t)C_j^{[\alpha]}(t)\boldsymbol{\mu}_{ij}(\mathbf{R}^{[\alpha]}(t))] \tag{10}$$

is able to produce a monotonous population increase (or decrease) of a target state i, $(|C_i(t)|^2)$, which in turn can induce the desired surface hop toward the same state. This method can be used to drive a particular molecular system into an excited state of interest, which, due to its particular electronic configuration, is able to trigger a specific chemical process.[35]

■ APPLICATIONS

Simulation of Experimental (Time-Resolved) Observables

The advent of femtosecond lasers made it possible to observe chemical reactions on a time scale shorter than one bond vibration. In femtosecond spectroscopy, a first laser pulse excites the system of interest, while a second laser probes the evolution of the same system as a function of the time delay between the two pulses. This pump−probe approach is mostly implemented in the optical domain, and as a result, it cannot deliver molecular structural data due to the wavelength of visible−UV light. On the other hand, X-ray diffraction and X-ray absorption spectroscopies such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) are able to give structural details at atomic resolution due to their short wavelengths (on the order of an angstrom). Until recently, radiation sources operating at these wavelengths were unable to produce pulses on the ultrafast time scale. However, modern synchrotrons and the recent X-ray free electron lasers (XFEL) are now able to produce high intensity X-rays on the pico- and femtosecond time scales. In addition, XFEL pulses are of the order of 1 million times brighter than third generation synchrotron light sources making therefore single shot experiments feasible. These new advances create the possibility for a large range of exciting new investigations in the field of time-resolved structural dynamics.

The rapid development of these experimental techniques requires however a parallel refinement of those theoretical approaches required for the correct interpretation of the measured observables. In Figure 1, I report the experimental and theoretical X-ray absorption spectra of the K- and $L_{2/3}$-edges of iron tris-bipyridine ($[Fe(bpy)_3]^{2+}$).[36] The agreement between the results is such that one can safely use the theoretical electronic structure calculations to compute the assignments associated with the different transitions. This is a clear example of the possible synergy between theory and experiment: the complexity of the calculations requires a constant validation of the theoretical models (the K-edge is best computed with TDDFT, while the $L_{2/3}$-edge is evaluated with DFT/ROCIS[37]); on the other hand, the theoretical model offers a unique way to guide the interpretation of the different bands in terms of state and orbital transitions.

Finally, with the advent of new technologies (in particular FEL applied to liquid jets), it may become possible to study the dynamics of these and other similar complexes in explicit solvents with a time resolution in the sub-picosecond time scale.[39]
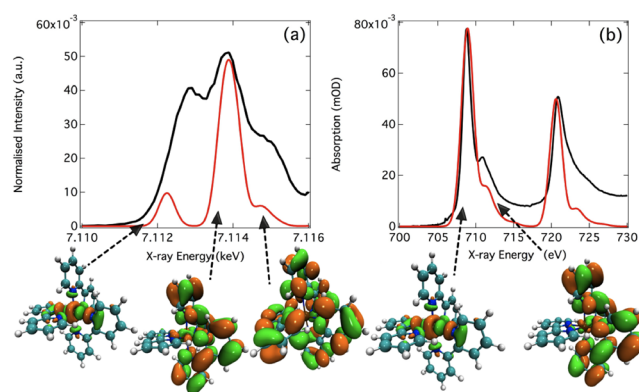

Figure 1. (a) Pre-edge region of the Fe K-edge in $[Fe(bpy)_3]^{2+}$ and (b) $L_{2/3}$-edge spectrum for low spin. The important molecular orbitals are shown beneath. Black curves, experiment;[38] red curves, theory.

Ultrafast Dynamics of Photoexcited Metal Complexes at Atomistic Resolution

Tris(bipyridine) metal compounds are the *hydrogen atom model* of the metal-to-ligand charge transfer (MLCT) complexes. The photophysics of these systems consists first in a stimulated singlet-to-singlet transition of one electron from the central metal atom into the ligand system ($(bpy)_3$) followed by an ultrafast intersystem crossing to a triplet state (also of MLCT nature). While in the gas phase the excited electron distributes uniformly among the three ligands, in solution the situation is rather different. In fact, the very peculiar and anisotropic arrangement of the first two to three solvation shells together with the ultrafast reorientation of the individual dipoles in the bulk causes, in the case of water,[40,41] a clear localization of the excited electron on mainly one (but sometimes two) ligands. In the case of water, the first solvation shell is arranged into a linear chain of hydrogen bonded water molecules organized along the grooves between the ligands. The water molecules of the chain are free to rotate along the O−H bond involved in the one-dimensional hydrogen bond network, offering therefore the possibility of an ultrafast (i.e., nondiffusive) reorientation of the molecular dipoles. Clearly, the level of detail needed for the description of this highly organized solvent structure requires the use of an atomistic representation of the solvent. A coarse-grained or implicit description of the solvent will miss some of the important effects induced by the solvent dynamics and therefore is not appropriate to give an accurate account of the detailed structural reorganizations that influence the dynamics of the MLCT complex in the sub-picosecond time scale. Using TDDFT-based TSH dynamics, we are able to describe the ultrafast intersystem crossing (ISC) dynamics that follows the photoexcitation of ruthenium(II)tris-(bipyridine), $[Ru(bpy)_3]^{2+}$, in water.[42] Upon excitation, the system reaches one of the bright singlet MLCT states from which it relaxes through internal conversion into the lower lying singlet states (Figure 2).

This first part of the dynamics is very fast (<100 fs) and leads to several ISC events with the triplet states in agreement with the results of experiments performed on similar compounds.[43] The mechanism underlying this ultrafast dynamics can be easily understood from our atomistic TSH calculations in explicit solvent. After excitation, the electron promoted into the ligand system (mainly localized on a single bipyridine moiety) is stabilized through the dipole reorientation of the water molecules in the first solvation shell (Figure 3). Due to the
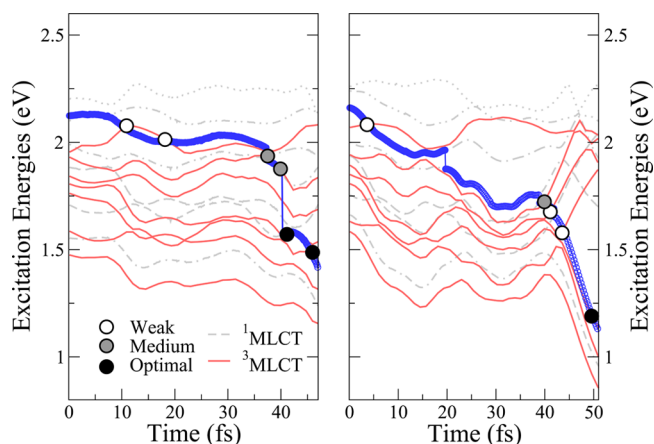
Figure 2. Nonadiabatic molecular dynamics of $[Ru(bpy)_3]^{2+}$ in solution. The panels show the time series of the relevant excited state energies corresponding to two representative trajectories. Singlet excited states (seven in total) are represented by gray dashed lines and triplet states (seven in total) by red continuous lines. The driving state is highlighted with blue circles. Analyzed crossings between singlet and triplet states are represented by filled circles with the following color coding: white = weak, gray = medium, and black = large SOCs. Adapted with permission from ref 42. Copyright 2011 Elsevier.
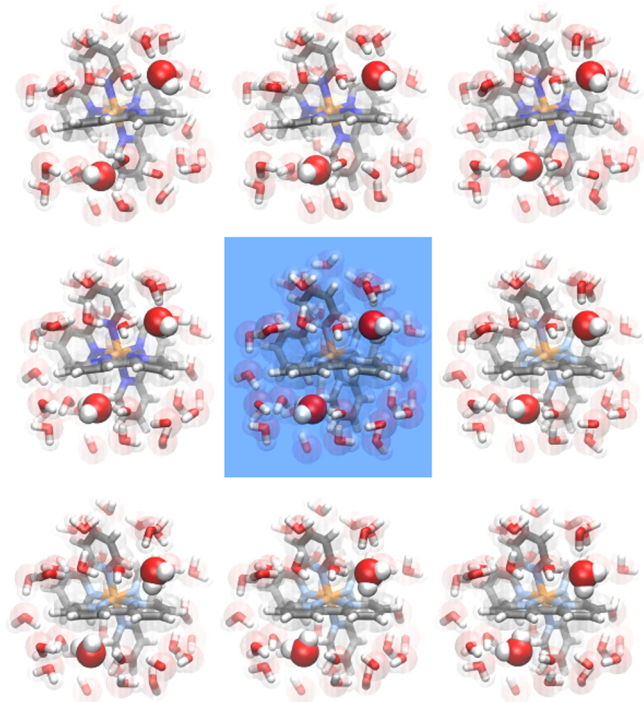

Figure 3. TDDFT-TSH dynamics of $[Ru(bpy)_3]^{2+}$ in solution. The different snapshots show the time evolution of the system at −120, −100, −60, −20, 0, 12, 25, 32, and 50 fs before and after the photoexcitation that occurs at time 0 (frame with blue background). The frames are ordered from the upper left corner to the lower right corner of the picture. The ligand that acquires the larger fraction of the excited electron (>80%) is the one pointing toward the reader. After excitation, the two water molecules (in van der Waals representation) are rapidly reorienting, pointing their dipoles toward the ligand carrying the extra electron.

size of the spin−orbit coupling between the lower lying singlet and triplet MLCT states, the ^{1}MLCT → ^{3}MLCT transition is completed in about 50−80 fs in all trajectories. Once more, the

use of accurate *ab initio* molecular dynamics calculations is key to the interpretation of the experimental results and allows for a detailed explanation of the intra- and intermolecular mechanisms governing this complex photophysical process. However, a word of caution is necessary regarding the use of TSH in the simulation of large molecular systems. In most cases, the large computational costs associated with these calculations limit the number of trajectories drastically (in the order of a few tenths). This implies that in the case of multiple reaction channels this approach will not reproduce the correct branching statistics in configuration space; nonetheless, in many cases the slope of the relevant PESs at the Franck−Condon region is such that the reaction path is well defined (with only few branches) at least during the first few hundreds femtoseconds of dynamics.

The long-term dynamics (in the picosecond time scale) of the triplet MLCT complex can also be followed using *ab initio* molecular dynamics simulations.[41] In this case, adiabatic Born−Oppenheimer dynamics in the lowest triplet state can already provide an accurate account of the spin density dynamics in the ligand system, disclosing the detailed time evolution of the photoexcited electron. The analysis of these trajectories shows a localization of the MLCT electron on mainly one ligand with sporadic extensions toward a second one; this peculiar electronic configuration (which differs from the homogeneous distribution over the three ligands observed in gas phase) is stabilized through the orientation of the water dipoles in the bulk, which overall produces a stabilizing electric field of about 1 V (see Figure 4).[41]
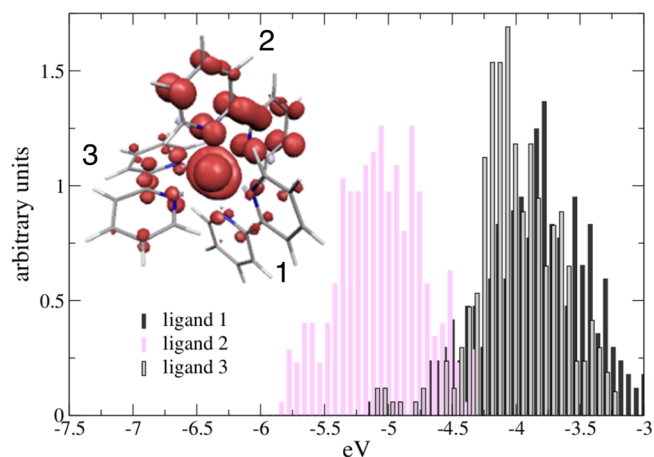

Figure 4. Electrostatic potential distributions computed from the excited state dynamics of $[Ru(bpy)_3]^{2+}$ in water. The potential generated by all (3298) solvent molecules is evaluated at the center of mass of each ligand (labeled with indices 1, 2, and 3, see inset). The ultrafast nondiffusive relaxation of the bulk water induces a stabilization of about 1 eV of the excited MLCT electron on ligand 2. The inset on the left shows the spin density computed for a representative frame.

Pulse Shaping and Modeling of Chemical Reactions

Optimal control theory deals with the design of optimal pulses for the attainment of desired chemical reactions. In practice, this is achieved through a *nondeterministic* optimization procedure based for instance on genetic algorithms, which solve the problem of driving a chemical reaction toward a given product without using specific physicochemical information about the system itself. The development of more accurate theoretical models for the description of the complex electron−
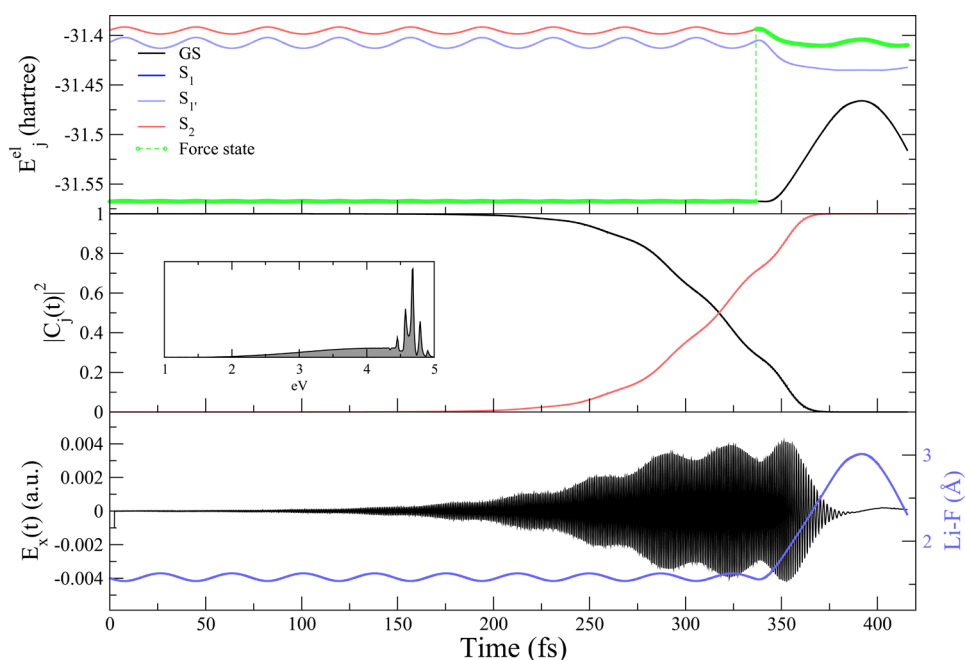
Figure 5. TDDFT-based TSH combined with local control for the selective excitation of LiF into the second singlet excited state, S_2. (upper panel) Time series of potential energy curves. The state that drives the dynamics is shown in green. (middle panel) States populations; for this trajectory, we achieved full population transfer to S_2 within 400 fs. The inset reports the Fourier transform of the LCT pulse. (lower panel) LCT pulse in the time domain. The blue line shows the evolution of the LiF bond length.

nuclear dynamics in the excited states offers the opportunity to study the pulse shaping process in a fully *deterministic* manner, providing valuable information about the meaning and the implications of the different frequencies composing the final pulse. Of course, due to the number of approximations required for an efficient simulation of the nonadiabatic processes in the presence of explicit time-dependent electric fields, we do not expect that the theoretically produced pulses can be effectively used to drive chemical reactions in the laboratories. Nonetheless, we believe that the information that can be recovered from the analysis of the theoretical pulses can help shed new light on the effects of the different frequency components on the overall chemical reaction path leading to the desired product, opening new possibilities for a rationalization of the optimization process.

The local control algorithm described in the theory section is a very simple pulse shaping procedure that can be easily combined with TDDFT-based TSH dynamics.[35] The outcome of this type of simulation is an effective laser pulse that induces the selective population of a desired reactive excited state. Using this method, we can therefore explore the reaction channels associated with the different excited states and provide a way to induce chemical reactions by means of designed laser pulses. This approach can be further improved by including the possibility of mixing time-delayed pulses (in the vis/UV but also IR frequency range) that produce a series of controlled electronic transitions, which can trigger more complex and rich chemical reactions.

As a proof of principle, in Figure 5, I report the dynamics of photoexcited LiF together with the LCT pulse obtained on-the-fly using TDDFT-based TSH dynamics. In this specific case, we targeted the second singlet excited state (S_2), which corresponds to an excited bound state that does not lead to bond dissociation (but rather to a bond elongation).

While the use of these "theoretically" designed pulses in real experiments is still questionable (because of the many approximations intrinsic to these calculations, like the use of classical independent trajectories and approximated DFT functionals), the strengths of this approach is at least twofold: (i) It allows a direct excitation of the system starting from a ground state simulation; this constitutes an important step forward compared with the usual practice of switching, instantaneously, the forces acting on the system from the ground state to the excited state. In LCT, the excitation is obtained through the smooth transfer of population from the ground state to the selected excited state (middle panel in Figure 5). (ii) The analysis of the pulse allows for the identification of the most important vibrational modes involved in the chemical process triggered by the population of the selected excited state. The inspection of the pulse frequencies (see inset of Figure 5) and their analysis in terms of effective modes can be used to rationalize the physics of the excitation process, opening new possibilities for the control of complex chemical reactions in the excited states.

For instance, TDDFT-based TSH/LCT dynamics can be applied to the study of the intramolecular proton transfer reaction in organic molecules. In this case, the reaction is triggered through the selective population of the molecular orbital that carries the larger antibonding character at the proton donating group. An application of this strategy is currently under investigation.

■ CONCLUSIONS

In this paper, I have described the most recent advances in TDDFT-based nonadiabatic molecular simulations for applications in the study of the excited state dynamics of realistic systems. By "realistic", I mean molecular systems in their full atomistic representation evolving in ambient conditions that closely match the ones encountered in experiments. This

includes an accurate characterization of the electronic structure of the ground and excited states, the description of the molecular dynamics in its full unconstrained configuration space, and an adequate representation of the interaction with the environment at atomistic level (using either DFT or classical molecular mechanics). As shown in different applications, the solvent can play an important role in photoactivated chemical processes: it can react electronically with the excited solute molecule as in the case of highly ionized molecules in solution,[44−46] or it can fine-tune the electrostatic potential in the neighborhood of the solute through a reorganization of the hydrogen-bond network like in the case of dyes in solution. A detailed atomistic description of the environment is therefore an essential ingredient in the study of the *photodynamics* of molecular systems in solution.

Mapping experimental time-resolved low-dimensional observables (one- or two-dimensional absorption spectra) into the dynamics in the $3N_n$ dimensional configuration space is done at best with the help of numerical simulations of the underlying dynamics, which has to accurately match all experimental conditions (solvent effects, temperature, pressure, concentration, etc.). However, the inverse of this mapping, which consists in the reproduction of experimental spectra from numerical simulations is also of paramount importance for the optimal *tuning* of those parameters that inevitably characterize any numerical calculation of complex systems for which the corresponding time-dependent Schrödinger equation of both electron and nuclear degrees of freedom cannot be solved exactly. The synergy between experiments and theory needs therefore to be pushed forward in the attempt to increase the understanding of the exciting new physics at short space and time resolutions.

As shown in the many applications of the TDDFT-based nonadiabatic molecular dynamics schemes developed in the recent years, once a good accuracy of the electronic structure (for ground and excited states) and of the underlying quantum nuclear dynamics is reached, these numerical approaches will allow the simulation of complex chemical and physical processes with a good level of *predictivity*. Predictivity is indeed the ultimate goal of most advanced *ab initio* molecular dynamics approaches. Moving further, I believe that the time is ripe for pushing simulations into the realm of molecular design.[47] While predictivity requires *ab initio* MD simulations to reproduce properties and dynamics of molecular systems given a satisfactory (and experimentally proven) representation of the molecular Hamiltonian and of the corresponding dynamics, molecular design requires a further *extrapolation* step, which allows us to extend predictivity into regions of the chemical compound space that were never sampled before. This is probably the greatest theoretical challenge for the next decades, possibly combining *ab initio* MD simulations with new nondeterministic approaches such as machine learning, data mining, and evolutionary algorithms.

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Notes

The authors declare no competing financial interest.

Biography

Ivano Tavernelli was born in 1967 in Mendrisio, Switzerland. He studied Biochemistry (M.Sc., 1991) and then Theoretical Physics (M.Sc., 1996) at the Eidgenossische Technische Hochschule Zurich (ETHZ), where he also obtained his Ph.D. in 1999. In 2000, he received a Marie Curie Fellowship and went to work in the group of Prof. Michiel Sprik in the department of Chemistry at Cambridge University (U.K.), where he stayed until 2002. He then moved back to Switzerland to join the group of Prof. Ursula Röthlisberger, first at ETHZ (2002−2003) and later at the Ecole Polytechnique Fédérale de Lausanne (EPFL, 2003 until now). In 2010, he earned the title of Maitre d'Enseignement et de Recherche (MER) at EPFL. In the field of quantum-classical dynamics, Ivano Tavernelli has developed novel theoretical frameworks able to combine electronic structure techniques based on density (DFT and TDDFT) with the calculation of nonadiabatic quantum and classical trajectories. His research interests comprise adiabatic and nonadiabatic molecular dynamics (Ehrenfest dynamics, trajectory surface hopping, and Bohmian dynamics) for the study of photochemical and photophysical processes in molecules, condensed phase, and biological systems.

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